Proceedings of the European Conference Physics of Magnetism, Poznań 2014

Multiband *d–p* Model for the Description of Sr_2RuO_4

K. Rościszewski[a,*] and A.M. Oleś[a,b]

[a]Marian Smoluchowski Institute of Physics, Jagiellonian University, W.S. Reymonta 4, PL-30-059 Kraków, Poland
[b]Max-Planck Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

We study electronic structure of multiband d–p model describing RuO_4 layer such as realized in Sr_2RuO_4. The model takes into account nearest-neighbor anisotropic ruthenium–oxygen and oxygen–oxygen hoppings, intra-atomic Coulomb interaction, Hund's exchange and in addition spin–orbit coupling on ruthenium. The RuO_4 is universally considered as a pure t_{2g} system (with e_g orbitals empty) due to sizable gap between t_{2g} and e_g levels. We show that ruthenium e_g orbitals are in fact occupied, similarly like showed earlier for CoO_2 layers.

DOI: 10.12693/APhysPolA.127.260

PACS: 75.25.Dk, 75.47.Lx, 71.70.Ej

1. Introduction

The description of d-orbitals physics in transition-metal-oxides in general is a difficult task. Systems with completely filled t_{2g} orbitals and not fully occupied and therefore active e_g orbitals are much easier to study. Similarly, the systems with completely empty e_g orbitals and the active t_{2g} orbitals are also much easier. Such systems can be realized if t_{2g} to e_g gap (induced by crystal-field effects) is large. The system which is commonly believed to belong to this class is Sr_2RuO_4 (due to large $\approx$3 eV gap [1]). However there are some doubts if indeed such simplified scenario is realized in many transition-metal-oxides. First, there were *ab initio* cluster+embedding computations by Kaplan and Soullard [2] who claim that: (i) the p-orbital charge on oxygens (in Sr_2RuO_4) is not formally 6 but is rather closer to 5.0; (ii) the occupation on d orbitals is close to 6 (not to formal 4); (iii) e_g levels are occupied; (iv) charges on strontium ions are not formal 2^+ but rather are $\approx 1.6^+$.

Similarly, CoO_2 layers were also commonly believed to be pure t_{2g} systems. However, in quite recent publication [3] it was shown that e_g orbitals are in fact very important.

2. Theory

To solve the dilemma about e_g levels in Sr_2RuO_4 we performed unrestricted Hartree–Fock computations on small quasi-two-dimensional cluster which contains 16, i.e. 4×4 Ru ions and 64 oxygens: 32 located in-plane, and 32 out-of-plane apical oxygens. The effective Hamiltonian consists of several parts

$$\mathcal{H} = H_{\rm kin} + H_{\rm so} + H_{\rm diag} + H_{\rm intra}. \tag{1}$$

The kinetic (hopping) part of the Hamiltonian is

$$H_{\rm kin} = \sum_{\{i,\mu;j,\nu\},\sigma} t_{i,\mu;j,\nu} c^{\dagger}_{i,\mu,\sigma} c_{j,\nu,\sigma} + \text{H.c.}, \tag{2}$$

where a general notation $c_{j,\nu,\sigma}$ for the annihilation operator is used (j is the site number, ν labels orbitals, and $\sigma =\uparrow,\downarrow$ spins; alternatively for d-orbitals we can write $d_{j,\nu,\sigma}$, while for p-orbitals $p_{j,\nu,\sigma}$).

The matrix $t_{i,\mu;j,\nu}$ is assumed to be non-zero only for nearest-neighbor atoms; they are obtained using the Slater–Koster rules [4] (see the Table).

TABLE

The oxygen-ruthenium hopping elements in RuO_4 plane obtained using Slater–Koster rules [4]: $(pd\pi)$ and $(pd\sigma)$ are the Slater–Koster interatomic integrals. Oxygens positions in RuO_6 octahedron can be pointed out by vectors $\pm\boldsymbol{a}_1 = \pm a(1,0,0)$, $\pm\boldsymbol{a}_2 = \pm a(0,1,0)$; the apical oxygen positions by $\pm\boldsymbol{a}_3 = \pm b(0,0,1)$. The vector $\boldsymbol{R} = \boldsymbol{R}_i - \boldsymbol{R}_j$ is the jump vector from j-th oxygen (at $\boldsymbol{R}_j$) to i-th ruthenium. The symbols $(l,m,n) = (\frac{R_x}{R}, \frac{R_y}{R}, \frac{R_z}{R})$ are direction cosines of the jump.

$\boldsymbol{R}$	(l,m,n)	ν	μ	$t_{j,\nu;i,\mu}$
$\pm\boldsymbol{a}_1$	$(\pm1,0,0)$	x	x^2-y^2	$l(\frac{\sqrt{3}}{2})(pd\sigma)$
$\pm\boldsymbol{a}_1$	$(\pm1,0,0)$	x	$3z^2-r^2$	$-l(\frac{1}{2})(pd\sigma)$
$\pm\boldsymbol{a}_1$	$(\pm1,0,0)$	y	xy	$l(pd\pi)$
$\pm\boldsymbol{a}_1$	$(\pm1,0,0)$	z	zx	$l(pd\pi)$
$\pm\boldsymbol{a}_2$	$(0,\pm1,0)$	y	x^2-y^2	$-m(\frac{\sqrt{3}}{2})(pd\sigma)$
$\pm\boldsymbol{a}_2$	$(0,\pm1,0)$	y	$3z^2-r^2$	$-m(\frac{1}{2})(pd\sigma)$
$\pm\boldsymbol{a}_2$	$(0,\pm1,0)$	x	xy	$m(pd\pi)$
$\pm\boldsymbol{a}_2$	$(0,\pm1,0)$	z	yz	$m(pd\pi)$
$\pm\boldsymbol{a}_3$	$(0,0,\pm1)$	z	$3z^2-r^2$	$n(pd\sigma)$
$\pm\boldsymbol{a}_3$	$(0,0,\pm1)$	x	xz	$n(pd\pi)$
$\pm\boldsymbol{a}_3$	$(0,0,\pm1)$	y	yz	$n(pd\pi)$

Simplified spin–orbit part of the Hamiltonian $H_{\rm so}$ formally is similar to kinetic part of the Hamiltonian [5][†]

*corresponding author; e-mail: krzysztof.rosciszewski@uj.edu.pl

[†]The derivation of spin–orbit starts from a single-site model. Using $|i,\mu,\sigma\rangle$ basis one evaluates the full matrix of scalar product $\langle i,\nu,\sigma'|\boldsymbol{L}_i \cdot \boldsymbol{S}_i|i,\mu,\sigma\rangle$ of angular momentum with spin operator $\boldsymbol{L}_i \cdot \boldsymbol{S}_i$ (at the site i). The elements of single-site $H^i_{\rm so}$ can be chosen as hopping-elements $t_{i,\nu,\sigma';\mu,\sigma} d^{\dagger}_{i,\nu,\sigma'} d_{i,\mu,\sigma}$ (between different spins and orbitals) with $t_{i\nu,\sigma';\mu,\sigma}$ such that they reproduce previously evaluated matrix elements. However when coming from one-site one-particle wave functions to true global wave function then the above derivation becomes rather an educated guess

with off-diagonal t-elements restricted to single ruthenium sites. As we use real d basis several spin–orbit elements turn out to be purely imaginary (therefore we will have to work with a general complex Hermitian Hamiltonian, not with a simple real and symmetric matrix). The elements of the matrix $t^{\rm so}$ for an i-th site are the following (compare Fig. 6 in Ref. [6]):

$$H^i_{\rm so} = \frac{\zeta}{2} \times \begin{bmatrix} 0 & 0 & 0 & 2\mathrm{i} & 0 & 0 & 1 & -\mathrm{i} & 0 & 0 \\ 0 & 0 & \mathrm{i} & 0 & 0 & -1 & 0 & 0 & -\mathrm{i} & -\sqrt{3}\mathrm{i} \\ 0 & -\mathrm{i} & 0 & 0 & 0 & \mathrm{i} & 0 & 0 & -1 & \sqrt{3} \\ -2\mathrm{i} & 0 & 0 & 0 & 0 & 0 & \mathrm{i} & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{3}\mathrm{i} & -\sqrt{3} & 0 & 0 \\ 0 & -1 & -\mathrm{i} & 0 & 0 & 0 & 0 & 0 & -2\mathrm{i} & 0 \\ 1 & 0 & 0 & -\mathrm{i} & -\sqrt{3}\mathrm{i} & 0 & 0 & -\mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 1 & -\sqrt{3} & 0 & \mathrm{i} & 0 & 0 & 0 \\ 0 & \mathrm{i} & -1 & 0 & 0 & 2\mathrm{i} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{3}\mathrm{i} & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \tag{3}$$

where ζ is the strength of the spin–orbit coupling and where the columns and rows are numbered in the following order: $xy\uparrow$, $yz\uparrow$, $zx\uparrow$, $x^2-y^2\uparrow$, $3z^2-r^2\uparrow$, $xy\downarrow$, $yz\downarrow$, $zx\downarrow$, $x^2-y^2\downarrow$, $3z^2-r^2\downarrow$.

The next part of the Hamiltonian $H_{\rm diag}$ depends only on particle operator numbers and takes into account the effects of crystal field and the difference of reference energies ε_p between empty d and empty p orbitals (we fix reference energy ε_d for d orbitals to zero, hence the p index in ε_p):

$$H_{\rm diag} = \sum_{i,\mu=x,y,z;\sigma} \varepsilon_p(i) p^\dagger_{i,\mu,\sigma} p_{i,\mu,\sigma} + \sum_{i,\mu=xy,yz,\ldots;\sigma} f^{\rm cr}_{\mu,\sigma} d^\dagger_{i,\mu,\sigma} d_{i,\mu,\sigma}. \tag{4}$$

(The first sum is restricted to oxygen sites, while the second runs over ruthenium sites.)

The local Coulomb interaction Hamiltonian for d-orbitals in multi-band Hubbard model is [5]:

$$H^d_{\rm int} = U_d \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} + \frac{1}{2} \sum_{i,\mu\neq\nu} \left(U_d - \frac{5}{2} J^d_{\mu\nu} \right) n_{i,\mu} n_{i,\nu} - \sum_{i,\mu\neq\nu} J^d_{\mu\nu} \boldsymbol{S}_{i,\mu} \cdot \boldsymbol{S}_{i,\nu} - \sum_{i,\mu\neq\nu} J^d_{\mu\nu} d^\dagger_{i,\mu,\uparrow} d_{i,\nu,\downarrow} d^\dagger_{i,\mu,\downarrow} d_{i,\nu,\uparrow}, \tag{5}$$

where $J^d_{\mu\nu}$ is the tensor of on-site inter-orbital exchange elements (for the precise values of $J^d_{\mu\nu}$ elements, see for example Ref. [7]). The interaction Hamiltonian for oxygens (p-orbitals) has a similar form.

Let us note that in ruthenates the long-range interatomic Coulomb interactions are difficult to model. In the following we will take account of their influence simply by requiring that ionic charges are distributed in the crystal homogeneously, i.e. they can be attributed to one representative Ru ion and two representative oxygens (one in-plane and one out-of-plane apical oxygen).

We adopt in-plane d–p and p–p hopping elements $(pd\sigma)$, $(pd\pi)$, $(pp\sigma)$, $(pp\pi)$ used in Refs. [8–10]. For intra-site Coulomb repulsion on ruthenium sites U_d the value 3 eV is used while for Hund coupling J^d_H we use $J^d_H = 0.7$ eV [9, 11]. For intra-site Coulomb repulsion on oxygen sites (in ruthenates) we use $U_p = 4.5$ eV and $J^p_H = 0.6$ eV [12, 13]. The spin–orbit coupling on Ru sites is assumed to be 0.13 eV [14]. To complete the set of Hamiltonian parameters we must provide values for various crystal-field coefficients which we will adopt from various experimental references, to give an example the splitting between $t_{2\rm g}$ and $e_{\rm g}$ levels was fixed as 3.5 eV.

We will use the unrestricted mean-field HF approximation as described in Refs. [5, 8] and will look for homogeneous solutions.

3. Results

The results we obtain are the following: (i) the charge on oxygen-ions is not formal 6 but much lower; (ii) to obtain the formal occupation 6 on oxygens one must require that $U_p = 0$ and in addition ε_p must be negative and large.

We performed computations using two scenarios.

3.1. First scenario

First scenario is parallels idealistic, formal ionic model with 6 electrons per p-orbitals of each oxygen and 4 electrons per d-orbitals on Ru-ion. The assumed distribution

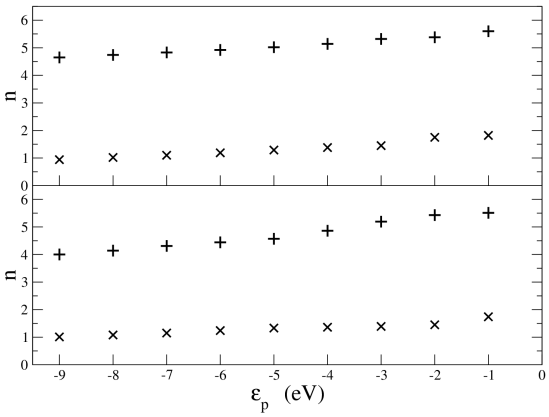

Fig. 1. Occupation numbers on ruthenium ion versus ε_p. Upper part (formal idealistic ionic model): there are $(4\times6+4)$ electrons per oxygen p-orbitals and ruthenium d-orbitals in a single RuO_4 unit. Lower part (more realistic model): there are $(4\times6+3)$ electrons per a single RuO_4 unit. The symbols + denote total occupation of ruthenium $t_{2\rm g}$ levels (i.e., xy, yz, zx orbitals) and the crosses × total occupation of $e_{\rm g}$ levels. Occupation numbers on oxygens are slightly higher than 5 (not shown; the apical oxygens have higher occupations).

of the charges is however not stable and under HF iterations they redistribute to give final result as shown in upper part of Fig. 1.

The ground state is ferromagnetic. (The paramagnetic state is metastable.) Finally spin–orbit contribution to energy is ≈−35 meV (on a single Ru). However, the real system has a paramagnetic ground state.

3.2. Second scenario

In the second scenario following what is reported in Ref. [2] we assume that two Sr ions donate to the RuO_4 layer not 4 but 3 electrons. We study a small cluster thus the true transfer charge (for two Sr ions) which is ≈3.2 must be clipped to 3. The results of the computations are shown in lower part of Fig. 1. The ground state is weakly-ferromagnetic and the occupation numbers we obtained are much closer to *ab initio* results.

4. Summary

Altogether the results are encouraging. We must add one note at the end. The e_g levels in both scenarios are occupied. However, one can guess that physical behavior of the system is governed mainly by the t_{2g} levels so the present results do not invalidate results reported in other papers obtained upon assumption that ruthenium-oxides are pure t_{2g} systems.

Acknowledgments

We kindly acknowledge support by the Polish National Science Center (NCN) under Project No. 2012/04/A/ST3/00331.

References

[1] K.T. Park, *J. Phys. Condens. Matter* **13**, 9231 (2001).

[2] I.G. Kaplan, J. Soullard, *Phys. Rev. B* **76**, 174505 (2007).

[3] K. Rościszewski, A.M. Oleś, *J. Phys. Condens. Matter* **25**, 345601 (2013).

[4] C. Slater, G.F. Koster, *Phys. Rev.* **94**, 1498 (1954).

[5] T. Mizokawa, A. Fujimori, *Phys. Rev. B* **54**, 5368 (1966).

[6] L.V. Poluyanov, W. Domcke, *J. Chem. Phys.* **137**, 114101 (2012).

[7] A.M. Oleś, G. Khaliullin, P. Horsch, L.F. Feiner, *Phys. Rev.* **72**, 214431 (2005); P. Horsch, in: *Handbook of Magnetism and Advanced Magnetic Materials*, Vol. 1, *Fundamentals and Theory*, Eds. H. Kronmüller, S. Parkin, Wiley, London 2007.

[8] T. Sugimoto, D. Ootsuki, T. Mizokawa *J. Phys. Soc. Jpn.* **82**, 104 (2013).

[9] T. Oguchi, *Phys. Rev. B* **51**, 1385 (1995).

[10] T. Mizokawa, L.H. Tjeng, G.A. Sawatzky, G. Ghiringhelli, O. Tjernberg, N.B. Brookes, H. Fuzakawa, S. Nakatsuji, Y. Maeno, *Phys. Rev. Lett.* **87**, 077202 (2001).

[11] Z.V. Pchelkina, I.A. Nekrasov, Th. Pruschke, A. Sekiyama, S. Suga, V.I. Anisimov, D. Vollhardt, *Phys. Rev. B* **75**, 035122 (2007).

[12] D.I. Khomski, M.V. Mostovoy, *J. Phys. A Math. Gen.* **36**, 9197 (2003).

[13] E. Arrigoni, M. Aichorn, M. Daghofer, W. Hanke, *New J. Phys.* **11**, 055066 (2009).

[14] C.N. Veenstra, Z.H. Zhu, M. Raiche, B.M. Ludbrook, A. Nicolaou, B. Slomski, G. Landolt, S. Kittaka, Y. Maeno, J.H. Dil, I.S. Elfimov, M.W. Haverkort, A. Damascelli, *Phys. Rev. Lett.* **112**, 127002 (2014).